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COCRYSTALLIZATION OF ULTRAMICRO QUANTITIES
OF IRON AND OTHER ELEMENTS WITH OXINE
GENERATED IN SITU

by
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ABSTRACT

The cocrystallization of iron in trace quantities with oxine formed homogeneously in solution by the hydrolysis of 8-acetoxyquinoline was studied. The distribution of microcomponent between the solid phase and the mother liquor was profoundly affected by the degree of supersaturation. After relief from supersaturation, a constant distribution coefficient was calculated by an equation which was predicated upon the Doerner-Hoskins equilibrium. The cocrystallization of other elements was also examined with an arbitrarily established set of conditions. Plutonium, cerium, and praseodymium were quantitatively recovered from solution.

SUMMARY

Determination of trace element abundances in seawater requires the concentration and ultimate isolation of an element from large quantities of salts and sample volumes. The cocrystallization of minute quantities of elements with certain organic reagents offers an effective means of achieving the separation.

The mechanism was explored by which trace amounts of iron cocrystallize with an organic reagent, oxine, which is formed homogeneously in solution. Further, a number of elements was screened to evaluate the general applicability of this system. The reagent carries plutonium, cerium and praseodymium quantitatively, and it seems likely that adjustment of variables would provide for application to a larger number of elements.

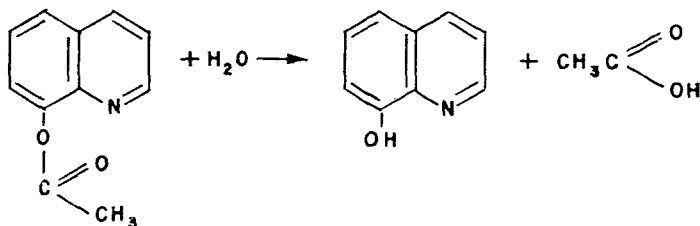
INTRODUCTION

In the cocrystallization process in which the entire quantity of both the organic reagent and trace element are present initially, the distribution of microcomponent between the crystalline phase and mother liquor in certain cases¹ obeys the Doerner-Hoskins logarithmic distribution law.² The law states that the microcomponent-carrier ratio of the crystal surface is proportional to the microcomponent-carrier ratio of the solution. Accordingly, the expression

$$\log \frac{M_f}{M_i} = \lambda \log \frac{C_f}{C_i}$$

is derived where M and C represent the microcomponent and carrier, i and f indicate initial and final quantities in solution, and λ is the logarithmic distribution coefficient.

This study examined the cocrystallization process in which the crystallizing compound is generated in situ and thereby promotes its own crystallization. The opportunity was provided by the recent description of the homogeneous formation of oxine in solution by the hydrolysis of 8-acetoxyquinoline.³



Consider a solution that contains the parent compound and an inorganic microcomponent capable of reacting with the hydrolytic product. When the water-soluble 8-acetoxyquinoline hydrolyzes in slightly alkaline medium, a condition in which oxine possesses limited solubility, crystallization of oxine occurs as its solubility is exceeded. With further hydrolysis, the rate of crystallization is governed by the rate of hydrolysis until the supply of the precursor compound is exhausted.

As in the mechanism of coprecipitation by Doerner and Hoskins, the surface of the crystallized material is considered to consist of oxine and oxinate which are in equilibrium with their counterparts in solution. This relationship can be expressed by:

$$\frac{(\text{Oxinate}) \text{ on surface}}{(\text{Oxine}) \text{ on surface}} = K \frac{(\text{Oxinate}) \text{ in solution}}{(\text{Oxine}) \text{ in solution}}$$

where K is a proportionality constant. With this equilibrium and the inverse relationship between the carrier solubility and the efficiency of cocrystallization, the removal of microcomponent from solution with the crystallized oxine can be expressed by

$$-\frac{dM}{dC} = \frac{kM}{S}$$

where k is the distribution coefficient and S represents the solubility of oxine. Integration of this expression with respect to the initial and final quantities in solution gives:

$$M = M_0 e^{-\frac{kC}{S}}$$

The applicability of this expression was studied in the cocrystallization of iron with oxine. Iron was used because it combines with oxine at the pH selected for the crystallization. Further, a preliminary examination indicated that the incorporation of this microcomponent proceeded at a rate which afforded close examination of the process.

A general survey was also made to determine application of this organic system to the separation of minute traces of elements from solution.

EXPERIMENTAL

The kinetics of hydrolysis was studied and a series of experiments were performed in which the recovery of iron with solid oxine was measured at various stages of hydrolysis.

Reagents

8-acetoxyquinoline (Burdick and Jackson Laboratories, Muskegon, Michigan): dissolved in n-butyl alcohol (AR) at a concentration of 220 mg/ml. This solution was prepared within a half-hour before use.

Ammonium carbonate (AR): saturated solution in distilled water. This solution was added to samples to neutralize the acetic acid formed in the hydrolysis of 8-acetoxyquinoline. The hydrogen ion concentration of samples was thereby maintained constant at pH 8.4-8.6.

pH 4.5 buffer solution: 8 g ammonium acetate (purified crystal) and 8 ml glacial acetic acid (AR) diluted to 2 liters with distilled water.

Oxine (Eastman Kodak): crystals.

Tracers

The following radioactive tracers were used in the form furnished by Oak Ridge National Laboratory (ORNL), Nuclear Science and Engineering Corporation (NSEC) or as prepared in the laboratory.

Pu²³⁷ (IV, in HNO₃ solution)
Ce¹⁴⁴-Pr¹⁴⁴ (III, in HCl solution; ORNL)
Zr⁹⁵ (IV, oxalate complex in oxalic acid solution; ORNL)
Sc⁴⁶ (III, in HCl solution; ORNL)
In¹¹⁴ (III, in HCl solution; ORNL)
Y⁹¹ (III, in HCl solution; ORNL)
U²³⁷ (VI, in HNO₃ solution)
Sn¹¹³ (chloride in HCl solution; ORNL)
Sb¹²⁴ (III, in HCl solution; ORNL)
Fe⁵⁹ (III, in HCl solution; ORNL)
Sr⁸⁵ (II, in HNO₃ solution; ORNL)
Mn⁵⁴ (II, in HCl solution; NSEC)
Os¹⁹¹ (in NaOH solution; ORNL)

Zn^{65} (II, in HCl solution; ORNL)
 Ag^{110} (I, in HNO_3 solution; ORNL)
 Nb^{95} (V, complex in oxalic acid; ORNL)
 Cr^{51} (III, in HCl solution; ORNL)
 Au^{195} (III, in HCl and HNO_3 solution; NSEC)
 Cs^{137} (I, in HCl solution; ORNL)
 Tl^{204} (I, in HNO_3 solution; ORNL)
 Ir^{192} (IV, Ir complex in HCl solution; ORNL)
 Co^{60} (II, in HCl solution; ORNL).

All the tracers were obtained commercially except U^{237} and Pu^{237} which were formed by the reactions $\text{U}^{236}(\text{n},\gamma) \text{U}^{237}$ at the Materials Testing Reactor and $\text{U}^{235}(\alpha,2\text{n}) \text{Pu}^{237}$ in the University of California 60-in. cyclotron. The purity of the radionuclides was established by gamma-ray pulse-height analysis. Some of the tracers contained inert carrier, and the quantities of carrier were limited so that their concentrations in a sample were 10^{-8} g/ml or less.

Method

Samples consisted of 1 ml of a radioactive tracer solution, 1 ml of ammonium carbonate solution, and 50 ml of water. They were equilibrated in test tubes for 15 minutes in a constant temperature bath maintained at either 0.0, 25.0, or $40.0^\circ\text{C} \pm 0.1^\circ\text{C}$. Then to each was added 1 ml of the 8-acetoxyquinoline solution. During an experiment samples were stirred constantly. Unless otherwise stated, to induce crystallization solutions were seeded with 0.39 ± 0.15 mg of oxine at a predetermined time after hydrolysis began. These times were 8, 12, and 30 minutes for experiments performed at 40, 25 and 0°C , respectively.

At certain times after the appearance of crystals, the samples were filtered rapidly through coarse-porosity sintered glass. Filtrates of the completely hydrolyzed samples were reserved for oxine solubility measurement. Other filtrates were discarded.

The crystalline phase was dissolved in approximately 10 ml of dilute acetic acid and the solution was collected in a test tube for the radioactivity measurement. After adjustment of the solution volume, a count was taken in a well scintillation counter for a duration sufficient to confine the counting error to 1 % or less. To determine the recovery of microcomponent, this count was compared with that of a radioactive control diluted to the same volume with dilute acetic acid.

Following radioactivity measurement, the solution was diluted with pH 4.5 acetate buffer and spectrophotometrically analyzed for oxine.

For oxine solubility determinations, the fully hydrolyzed filtrates were similarly diluted. The optical density measurements were made in a Beckman spectrophotometer at 252 m μ , the wavelength of maximum absorption. The relation between concentration and optical density adhered to Beer's Law (Table I). The standard deviation of measurements was about 2 %.

TABLE I

The Optical Density at 252 m μ of Different Concentrations of Oxine in Acetate Buffer (pH 4.5)

Oxine (μ g/ml)	Optical Density
1.0	0.216
2.0	0.443
4.0	0.905

RESULTS

The kinetics of hydrolysis for 8-acetoxyquinoline was determined indirectly by measurement of the quantity of oxine recovered in the solid phase at various intervals after crystallization. This information, together with the solubility of oxine at the respective temperature (Table II), could be used to determine the apparent quantity of reagent hydrolyzed. The hydrolysis rate is described by a first-order reaction with respect to 8-acetoxyquinoline concentration. (Fig. 1). The values which deviate from the line are attributable to supersaturation and therefore are excluded from consideration.

Cocrystallization Characteristics

The cocrystallization of Fe was studied during the course of hydrolysis. The distribution coefficients were calculated from the

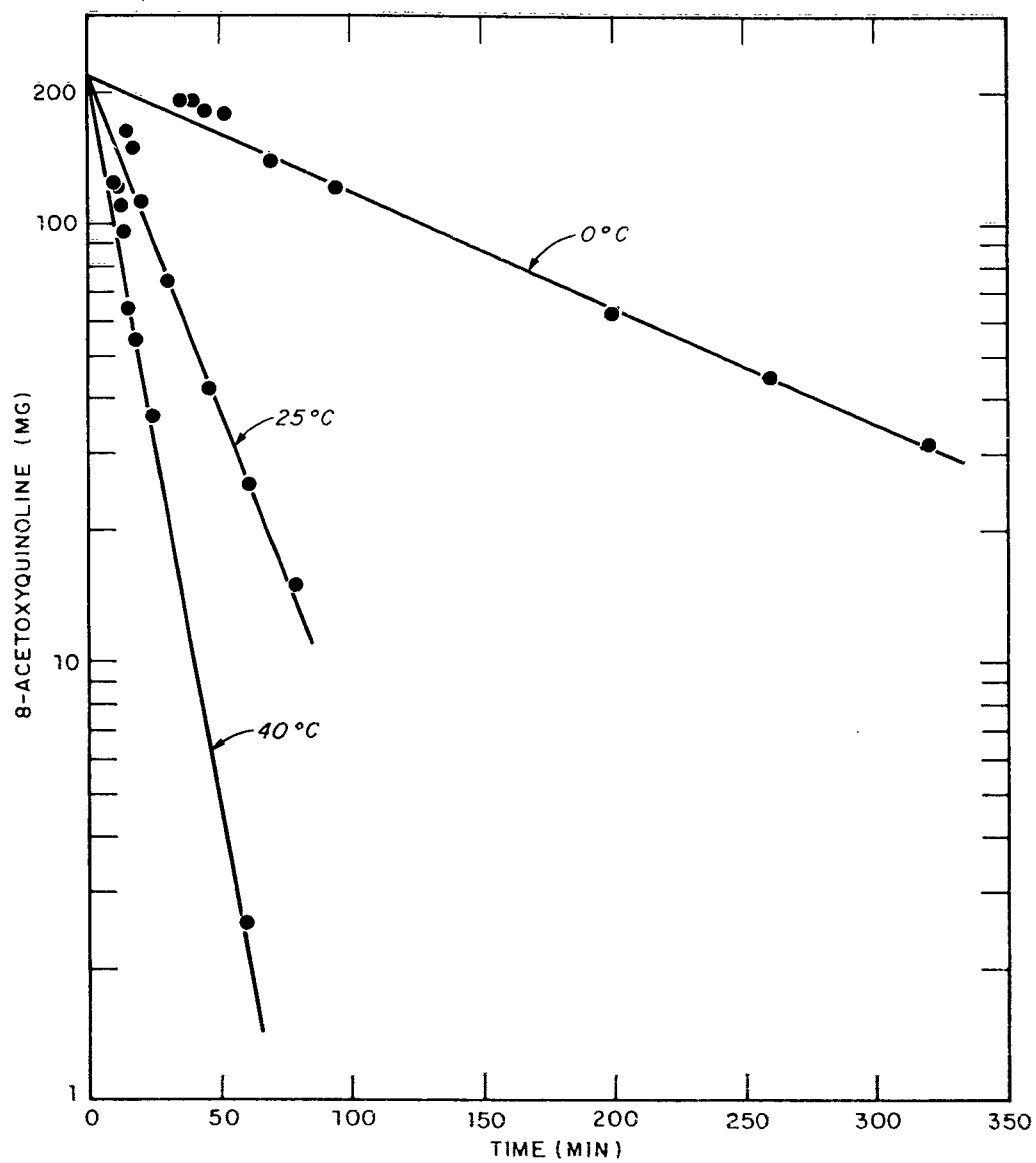


Fig. 1 The Hydrolysis of 8-Acetoxyquinoline at 0, 25 and 40°C.

TABLE II

Solubility of Oxine and Average Deviation

Temperature °C	Number of Determinations	Oxine in Completely Hydrolyzed Filtrate (mg/100 ml)
0	4	39.4 \pm 0.2
25	4	76.4 \pm 1.5
40	3	142.6 \pm 0.0

experimental data (Table III A). The value of the coefficient diminishes rapidly at first and approaches a more or less constant value as oxine recovery is increased.

Table IV shows the recovery of Fe upon stirring of the crystals in the mother liquor at 25 and 40°C for extended periods after the completion of hydrolysis. (The experiment was terminated at the times indicated because of the appearance of oxine degradation products). About 0.05 and 1.0 % of microcomponent is incorporated per hour at 25° and 40°C respectively after incorporation during active crystal formation.

The influence of seeding with oxine upon the distribution coefficient was evaluated by permitting three samples containing Fe tracer to hydrolyze for 25 minutes at 25°C. Two samples were seeded at 9 and 13 minutes after the beginning of hydrolysis and a third sample was allowed to crystallize spontaneously (18 minutes). At the end of the hydrolysis period, the quantity of crystals recovered from each of the samples was measured to be 65.5 mg. On the other hand Fe cocrystallized to the extent of 19.2, 29.3, and 42.6 % as the time between the initiation of hydrolysis and crystallization lengthened.

Table V shows the recovery of a variety of elements that cocrystallized with oxine at 25°C. The seed time was 12 minutes and crystals were collected 20 minutes after the start of the experiment. A wide range of recoveries was obtained, from values as low as 4 % for Cs, Ir and Co, to quantitateness for Ce, Pr, and Pu.

TABLE III A

The Cocrystallization of Iron With Oxine -
From Incipient Crystallization to Termination of Experiment

Hydrolysis Time (min)	M, Fraction of Iron Carried	C, Oxine Crystallized (mg)	S, Oxine in Solution ^a (mg/sample)	Distribution Coefficient $K = \frac{-\ln(1-M)}{C/S}$
<u>0°C</u>				
37.0	0.085	0.6	33.5	3.10
41.0	0.084	0.8	38.7	4.26
45.8	0.138	8.8	32.2	0.543
52.3	0.194	10.5	36.8	0.757
70.0	0.294*	41.9*	20.9	0.176
95.0	0.322	56.5	20.9	0.144
140.0	0.370	77.5	20.9	0.125
200.0	0.391	101.5	20.9	0.105
260.0	0.449	114.9	20.9	0.108
320.0	0.446	125.3	20.9	0.099
380.0	0.484	132.1	20.9	0.105
455.0	0.495	137.8	20.9	0.104
<u>25°C</u>				
14.25	0.085	2.8	60.0	1.90
14.50	0.088	5.5	58.1	0.973
16.25	0.234	15.2	55.7	0.527
20.0	0.360*	43.1*	40.9	0.423
30.0	0.382	72.4	40.9	0.271
45.1	0.393	97.8	40.9	0.209
60.0	0.390	111.1	40.9	0.182
80.0	0.414	119.5	40.9	0.183
<u>40°C</u>				
11.75	0.093	2.7	96.6	3.49
12.75	0.112	5.4	102.3	2.25
15.0	0.194*	41.4*	75.6	0.394
25.0	0.214	69.3	75.6	0.263
40.0	0.219	87.5	75.6	0.214
60.0	0.229	93.7	75.6	0.210

a. Calculated from the rate of hydrolysis and the quantity of crystallized oxine.

* The value of the first experimental interval after relief from supersaturation.

TABLE III B

The Cocrystallization of Iron With Oxine -
Corrected for Supersaturation

Iron Carried $M_{ss} = \frac{M-M^*}{1-M^*}$	Oxine Crystallized (mg) $C_{ss} = C-C^*$	Distribution Coefficient $K_{ss} = \frac{-\ln(1-M_{ss})}{C_{ss}/S}$	Standard Error ^b
<u>0°C</u>			
0.040	14.6	0.058	+ 0.017
0.108	35.6	0.067	+ 0.009
0.137	59.4	0.052	+ 0.005
0.220	73.0	0.071	+ 0.005
0.215	83.4	0.061	+ 0.004
0.269	90.2	0.073	+ 0.005
0.285	95.9	0.073	+ 0.005
	Av.	0.065	+ 0.007
<u>25°C</u>			
0.034	29.3	0.048	+ 0.019
0.052	54.7	0.040	+ 0.011
0.047	68.0	0.029	+ 0.009
0.084	76.4	0.047	+ 0.008
	Av.	0.041	+ 0.012
<u>40°C</u>			
0.025	27.9	0.069	+ 0.030
0.031	41.6	0.052	+ 0.018
0.043	52.3	0.064	+ 0.015
	Av.	0.062	+ 0.021

* The value of the first experimental interval after relief from supersaturation.

ss. Data corrected for supersaturation.

b. The standard error calculated by the usual formulas⁷ considered the determinate errors of counting (1 %) and oxine determination (2 %).

TABLE IV

The Continued Uptake of Iron by the Crystal
Phase After Complete Hydrolysis

Time After Initiation of Hydrolysis (hours)	Fraction Iron in Crystal
<u>25°C</u>	
24	0.419
48	0.426
114	0.475
<u>40°C</u>	
6	0.282
7	0.284
16.5	0.453
24	0.471

TABLE V

The CocrySTALLIZATION of Trace Elements With Oxine
(Temperature 25°C; Seed Time, 12 minutes; Hydrolysis
Time, 20 minutes)

Element	Fraction Recovered
Pu ²³⁷	1.00
Ce ¹⁴⁴	1.00
Pr ¹⁴⁴	1.00
Zr ⁹⁵	0.84
Sc ⁴⁶	0.71
In ¹¹⁴	0.62
Y ⁹¹	0.62
U ²³⁷	0.48
Sn ¹¹³	0.46
Sb ¹²⁴	0.40
Fe ⁵⁹	0.39
Sr ⁸⁵	0.20
Mn ⁵⁴	0.16
Os ¹⁹¹	0.11
Zn ⁶⁵	0.09
Ag ¹¹⁰	0.09
Nb ⁹⁵	0.09
Cr ⁵¹	0.08
Au ¹⁹⁵	0.06
Tl ²⁰⁴	0.05
Cs ¹³⁷	0.04
Ir ¹⁹²	0.04
Co ⁶⁰	0.04

DISCUSSION

The sequence of events during the isothermal hydrolysis of 8-acetoxyquinoline is shown schematically in Fig. 2. As this reagent hydrolyzes, the solution becomes supersaturated with oxine. Crystallization occurs spontaneously at critical supersaturation, or it is induced by seeding during the supersaturated phase with crystals of oxine. Supersaturation is relieved more or less rapidly, and upon its elimination the concentration of oxine in solution remains constant with time. During this stage of the process, the crystallization of oxine from solution proceeds at the rate of parent-compound hydrolysis.

The distribution coefficients calculated from the data (Table III A) show non-conformity with the Doerner-Hoskins equilibrium. For this equilibrium to be applicable to a system in which the crystallizable component is formed in situ, the solubility in the mother liquor must be unaltered during the entire course of crystallization. Clearly this prerequisite was not achieved (Fig. 2). The concentration of oxine in solution changed from the time of incipient crystallization until supersaturation was relieved. However this factor does not account for the nature of the variation in the distribution coefficient. The carrier solubility should be inversely related to the distribution coefficient, whereas, in fact, a converse relationship was determined experimentally.

Other investigators describe anomalous distributions coincident with supersaturation. For example in coprecipitation with basic stannic sulfate considerable contamination by manganese occurs in the early stages of precipitation during which the solution is supersaturated.⁴ It seems likely that in the present case crystallization from such a state is in some manner responsible for the inconstancy of the distribution coefficient. This view is substantiated by the profound influence of the degree of supersaturation, as controlled by seeding, upon the co-crystallization of iron. Conceivably, the metal-oxinate is concentrated in the crystal phase during the nucleation process. This suggestion would account for the observed effect of supersaturation when the direct relation between numbers of nuclei formed and degree of supersaturation⁵ is considered.

After the elimination of supersaturation, quantities of microcomponent continue to be incorporated by the crystal phase. According to Klein and Gordon,⁶ new nuclei are not formed during crystallization from homogeneous solution after supersaturation is relieved. This fact, together with constant solubility during this stage of the process,

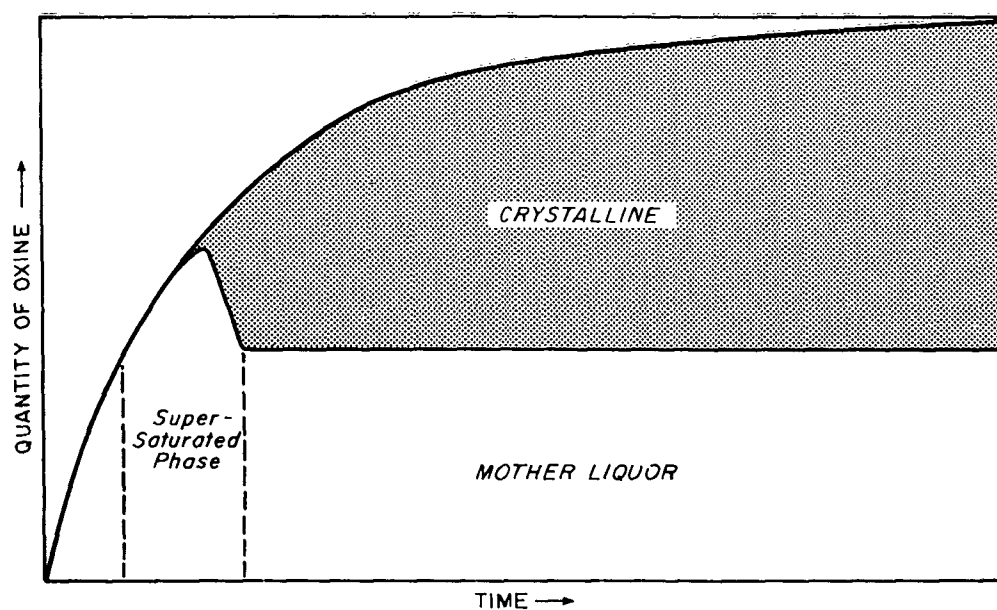


Fig. 2 The Formation of Oxine in Situ and Its Crystallization from Solution.

should be reflected by a constant distribution coefficient. To test the validity of this supposition, microcomponent was introduced into the system only after the elimination of supersaturation. The results of this experiment were complicated by the interaction of iron with the pre-formed solid phase, and this approach thereby offered no distinct advantage toward evaluation.

An alternative approach was examined in which the data shown in Table III A were re-computed in a manner designed to isolate the effect of supersaturation. The first experimental interval after which supersaturation is known to be relieved (Fig. 2) was considered the starting point, in calculating the recovery of oxine and microcomponent in the solid phase. Distribution coefficients were re-calculated on this basis and are shown in Table III B. The standard error, also shown, was calculated by usual statistical methods⁷ and considered the two errors, counting (1 %) and oxine determination (2 %). Other possible sources of error, namely the redistribution of iron as a result of recrystallization and diffusion, are regarded as unimportant. This conclusion follows from the magnitude of the effect of these factors upon incorporation of the trace element in systems where the pre-formed crystals were in contact with mother liquor for extended time periods (Table IV). Moreover, for the more dynamic system in which crystals are undergoing active growth the influence of these effects would be even further reduced.

While the magnitude of the standard error is large, particularly at the higher temperatures, it is clear that over a range of oxine recoveries the distribution coefficient is reasonably constant. Moreover while the solubility of oxine is vastly different at the three temperatures studied, the coefficients are consistent with one another. These results, therefore, substantiate the applicability of the Doerner-Hoskins equilibrium for the system described.

With regard to the recovery of elements from very dilute solution by cocrystallization with oxine (Table V), it should be emphasized that the conditions were arbitrarily established to give a general indication of the effectiveness of the method. In addition to providing for the efficient collection of Pu, Pr, and Ce from solution, it is probable that by adjustment of variables such as supersaturation, reagent concentration, temperature and hydrolysis time, the recovery of other elements can be enhanced and even brought within the region of quantitateness. As is evident, the method is non-selective but serves as a mechanism for concentration.

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NUCLEAR AND PHYSICAL CHEMISTRY BRANCH
N.E. Ballou, Head

CHEMICAL TECHNOLOGY DIVISION
L.H. Gevantman, Head

ADMINISTRATIVE INFORMATION

The work reported was done as part of a project for the Atomic Energy Commission. The project is described in this Laboratory's USNRDL Technical Program for Fiscal Years 1962 and 1963 (as revised January 1962) where it is designated Program A-5, Problem 8. Progress on the Project will be reported for the first time in the Quarterly Progress Report for the period 1 January to 31 March 1962.

Eugene P. Cooper

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Scientific Director

E. B. Roth

E.B. Roth, CAPT USN
Commanding Officer and Director

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